Rational design of new electrolyte materials for electrochemical double layer capacitors

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HIGHLIGHTS

- A systematic strategy for the design of EDLC electrolyte materials is presented.
- Large scale computational screening is followed by subsequent experiments.
- Cyanoesters are identified as new compound class for use as electrolyte solvent.
- Experimental validation proofs the usefulness of our approach.

ARTICLE INFO

ABSTRACT

The development of new electrolytes is a centerpiece of many strategies to improve electrochemical double layer capacitor (EDLC) devices. We present here a computational screening-based rational design approach to find new electrolyte materials. As an example application, the known chemical space of almost 70 million compounds is investigated in search of electrochemically more stable solvents. Cyano esters are identified as especially promising new compound class. Theoretical predictions are validated with subsequent experimental studies on a selected case. These studies show that based on theoretical predictions only, a previously untested, but very well performing compound class was identified. We thus find that our rational design strategy is indeed able to successfully identify completely new materials with substantially improved properties.

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1. Introduction

Electrochemical double layer capacitors (EDLCs) are electrochemical energy storage devices with substantial advantages considering cycle life, power density and charging-discharging time [1—4]. Their most critical property, the operative voltage, is limited by the stability of the electrolyte, which usually consists of quaternary ammonium salts like tetraethylammonium tetrafluoroborate (Et_4NBF_4) in organic solvents like propylene carbonate

(PC) or acetonitrile (ACN) [5—8]. Ionic liquids do allow for higher operative voltages [5], but their high viscosity and low conductivity limits their performance at room temperature (RT). The opportunities offered by organic solvents have furthermore not yet systematically investigated, though very promising results were achieved with for instance adiponitrile (ADN) [9]. One reason is that such studies are very resource intensive when done experimentally, which is why we have recently suggested to integrate computational screening methods with subsequent experimental studies to guide the development of new EDLC electrolyte materials [10,11]. The application of atom-scale computational methods is not new to the field [12—17], but large-scale screening approaches for electrolyte materials have been established only very recently [18—23], and only our earlier study presents experimentally validated results for EDLC electrolytes [10].

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Our screening approach makes use of methods from Quantum Chemistry, Chemoinformatics and Chemical Engineering to compute not only electrochemical stability window estimates, but also melting/flash/boiling points, viscosities, ion solubilities, pKas and further reactivity measures [18,19,22]. Using this approach to screen the 'toy system' of all reasonable, liquid nitrile solvents (almost 5000 compounds), ACN and ADN and a number of previously not investigated nitriles were found in the top10 list. Experimental investigation of two of the previously untested nitriles in the top10 list showed that also these nitriles performed well as electrolyte solvents [11]. Having a method at hand to pick promising candidates from systematically generated structure databases in a black box fashion, one is now in the position to systematically investigate the opportunities offered for designing new electrolytes based on organic liquids. The most crucial step is the setup of the "chemical space" of possible structures that are fed into the computational screening procedure. This "exploration" of chemical spaces is a well-known problem in computational drug design, where also organic molecules with specific physico-chemical properties are the target, though different properties are important. As a first step to make use of this knowledge for the development of new electrolyte materials, we have recently investigated the complete known chemical space, i.e. all compounds (about 70 million) which were reported to be made by chemists since such information is automatically fed into large databases like the PUBCHEM or CAS databases [22]. Our first analysis focused on identifying stable electrolytes that can provide desired solvation properties of the intermediates involved in lithium-air battery. The computational screening approach outlined above covers all relevant, basic properties of electrolyte solvents. For the case of lithium-air batteries, some of us had already identified a set of fundamental descriptors from this list, such as HOMO level, pKa, free energy of solvation of Li^+ and O_2^-, viscosity [24–28]. These (and many more) descriptors are now easily computable in large scale screenings and have already identified new promising electrolyte candidates. As a next step, we have made the computed data available to the community to explore novel ways for applications in electrochemistry. A key ingredient to enable discovery with the dataset is to provide users with a rich set of interaction and querying abilities. With this in mind, we have developed a tool termed SEED, System for Electrolyte Exploration and Discovery, which provides two ways for users to interact with the computed data, (i) visual exploration and (ii) natural language querying. The visual exploration tool allows for similarity and dissimilarity search, i.e. find trends that look similar or dissimilar to ones given by the user, respectively and representative and outlier search, i.e. find trends that are typical or anomalous, respectively. In the natural language querying scheme, users can directly query about the properties in natural language, for e.g. solvents with homo level less than −11.4 and with pKa in DMSO greater than 30. Given an electrolyte must satisfy many criteria simultaneously and often, these criteria are anti-correlated leading to multi-dimensional trade-offs that need to be taken into account when choosing an electrolyte. We believe candidate electrolytes identified through such systematic data-driven discovery will have a much higher likelihood of success than the Edisonian trial-and-error approach pursued currently.

In the following we present an analysis of this database with the goal of identifying new high-voltage electrolyte solvents for EDLCs, as well as experimental results for the validation of our theoretical predictions. This should serve as an example application case to illustrate how our approach can assist the development of new EDLC electrolyte materials and how it can help to gain further insight on organic liquid materials for electrochemistry.

2. Experimental

2.1. Computational screening

The following is a short summary of how the data was generated in our previous work, for details see the original publication [22]. Properties that were identified as crucial were: High electrochemical stabilities, suitable melting and boiling points, high flash points, low viscosities/high ion conductivities, and high ion solubilities (as well as low toxicity and cost). Estimates for these properties were computed with quantum chemical methods and the COSMOtherm model, with typical errors of about 5–10% and excellent correlation (R values close or above 0.9) between theoretical predictions and experimental measurements [10]. pKa values were computed as first measure of the general chemical stability of the compound for the most promising compounds.

Semi-empirical PM6-DH + [29,30] calculations were done with MOPAC2012 [31] making use of the COSMO solvation model [32] to generate the input for COSMOtherm (release C30-1501) [32]. BP86 [33,34] and B3LYP [35,36] DFT calculations have been performed with TURBOMOLE 6.4 [37,38], using D3 dispersion corrections [39], the RI approximation for two-electron-integrals [40,41] and again COSMO to generate input for COSMOtherm. Def2-TZVP atomic orbital basis [42] sets were employed throughout for TURBOMOLE calculations. Different conformations and vap. files were not taken into account. Doing so would mean a vast increase of computational work, which − as we mainly operate on semi-empirical level here − is unreasonable for the purpose of our study.

Structures were obtained from the PubChem Compound database, which comprised 67 million compounds at the time of retrieval. We then applied a hierarchical down-selection strategy to exclude all compounds which cannot be organic liquids due to elemental composition, very large size, etc. After additionally excluding all compounds for which high viscosity estimates were computed, almost 1 million (927,000) polar, organic liquids were left. SQM-level data is available for the full set. DFT-level data for the full set is in preparation and will also be released to the public. This set of compounds is analyzed here. Different strategies for doing this are possible, depending on the requirements that prospective new compounds have to meet.

Our final analysis in Section 3.1 focuses on suitable solvents with a high electrochemical stability, as we see the operative voltage as the most critical property. The final ranking listed only few commercially available compounds, from which we picked one especially promising candidate (a cyano ester) for experimental validation (see Section 3.2 for details) to illustrate the power of rational design approach.

2.2. Physical and electrochemical characterization

Based on the results of the computational screening, 3-Cyanopropionic acid methyl ester (CPAME, 99%, ABCR) was chosen for in depth electrochemical investigation. In a first step the solvent was dried over molecular sieve (3 Å) until its water content was below 25 ppm, as measured by Karl-Fischer technique. The conductive salt, tetraethylammonium tetrafluoroborate (Et_4NBF_4, Sigma-Aldrich), was added to the solvent until the maximum solubility was reached (0.6 mol dm^{-3} at 20 °C). Both storing of the solvent as well as the electrolyte preparation were done in a glove box (LabMaster, MBRAUN GmbH) with water and oxygen contents below 0.1 ppm.

The conductivity of the electrolyte was determined by performing impedance measurements with a Solartron model 1260 Impedance coupled with a potentiostat/galvanostat 273A PAR. A 0.01 mol dm^{-3} aqueous solution of KCl (VWR) was used to calibrate